

## Redox Flow Battery for Energy Storage

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**Abstract** The redox flow battery has undergone widespread research since the early 1970s. Several different redox couples have been investigated and reported in the literature. Only three systems as such have seen some commercial development, namely the all-vanadium (by VRB-ESS), the bromine–polysulfide (RGN-ESS) and the zinc–bromine (Powercell) systems. The vanadium–bromine system may be an attractive replacement for the all-vanadium system due to its higher energy density with possible applications as energy storage systems for electric vehicles. Other redox flow battery systems have faced problems due to slow electrochemical kinetics of redox couples, membrane fouling, cross-contamination, high costs (mainly due to the membrane as well as inefficient cell stack design), poor sealing, shunt current losses and low energy capacity (due to the use of aqueous electrolytes). One of the main factors limiting further development of the redox flow battery so far is the high costs associated with the ion-exchange membrane. Focussed research in this as well as areas such as reactor characterization and electrode design is necessary to ensure the widespread commercialization of the technology. In this paper, various redox

flow systems are discussed historically and technically and the latest developments are compared.

**Keywords** Redox flow battery · Redox couples · All-vanadium · Bromine–polysulphide

### الخلاصة

شهدت بطاريات الأكسدة والاختزال التدففية (redox flow batteries) أبحاثاً واسعة منذ أوائل السبعينيات. وقد تم التحقق والتوثيق لعدة أزواج من الأكسدة والاختزال (redox couples). وهناك فقط ثلاثة من هذه الأنظمة رأت بعض التطور التجاري، وهي كل الفاناديوم (بوساطة VRB-ESS)، والبرومين (فرة الخلية). وبالإمكان أن يكون نظام الفاناديوم – برومدين (زنك) – برومدين (فرة الخلية). وبالإمكان أن نظراً لكتافة طاقة خزن الطاقة العالية مع إمكانية استخدامه في بعض التطبيقات كأنظمة خزن للطاقة في المركبات الكهربائية. لقد واجهت أنظمة بطاريات الأكسدة والاختزال التدففية الأخرى معوقات يسبب بطيء الحركة الكهروكيميائية من أزواج الأكسدة والاختزال، وانسداد الأغشية، والتلوث الشامل، والنكافحة العالية (ويرجع ذلك إلى الغشاء إضافة إلى عدم كفاءة تصميم الخلية)، وضعف موائع التسرب، وفقدان تحويل التيار، وانخفاض سعة الطاقة (وذلك لاستخدام المحاليل الإلإكتروكيميائية المائية). إن أحد العوامل الرئيسية التي تحد من تطور بطارية الأكسدة والاختزال التدففية حتى الان هي الكلفة العالية المرتبطة بغشاء التبادل الأيوني. وبعد ترکيز البحث في هذا الموضوع إضافة إلى مواضع مرتبطة أخرى مثل توصيف المفاعل وتصميم الأقطاب من الضرورة بمكان وذلك لضمان التسويق التجاري لهذه التقنية. وقد تمت في هذه الورقة مناقشة أنظمة الأكسدة والاختزال المتعددة تاريخياً وتقريباً مع مقارنة آخر التطورات في هذا الموضوع.

### 1 Introduction

Research into renewable energy technology was spearheaded in the early 1970s as a reaction to various energy crises around that time. The costs of fossil fuels rose dramatically due to a shortage of supply [1]. Although these crises abated and interest in renewable energy declined during the 1980s, research efforts continued in this field, mainly due to increasing

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levels of carbon dioxide and other pollutants in the atmosphere causing global warming [2]. The so-called greenhouse gases are mainly emitted from fossil fuel-burning electrical power stations [1].

Due to the increasing demand for renewable energy, it is important to develop efficient energy storage systems that are able to store the uneven supply of energy when demand is low and to release it instantly when demand is high. This is called diurnal peak shaving or load leveling [3]. Energy storage systems are also used for [4,5]:

- utility ‘load leveling’ for conventional electricity generation;
- remote area power supply systems (RAPS);
- uninterrupted power supply (UPS) systems (for office buildings, hospitals and telecommunications);
- combined heat and power systems;
- industrial mobile power units such as warehouses, mines, submarines, etc.;
- traction (electric cars, trucks, buses, etc.).

Various technologies are available for utility-scale energy storage applications in the short to medium term [6,7]. These include secondary batteries, hydrogen fuel cells, fly-wheels, capacitors, and hydroelectric, electromagnetic and compressed air energy storage systems. Secondary batteries are attractive as stationary storage devices due to their rapid response times, high energy capacities and high storage efficiencies [5,8–10]. One such battery that has been widely

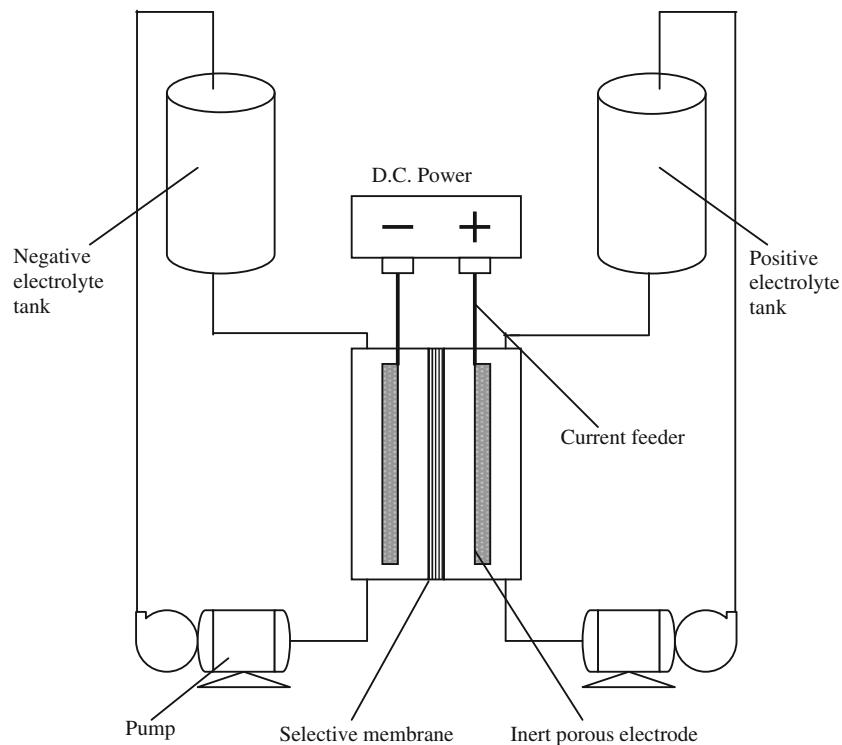
researched since the early 1970s is the redox flow battery [11].

In its simplest form, a redox flow battery consists of a positive and a negative half-cell separated by an ion-exchange membrane [12] as shown in Fig. 1. Each half-cell carries an inert electrode to enable electrical charge transfer in and out of the system. The electrolytes in each half-cell store the energy chemically as solutions and are pumped around the system. The electrolyte solutions contain electroactive species and a high concentration of an inert electrolyte to minimize the solution resistance. Each half-cell electrolyte is stored in a separate storage tank. There are two redox species with different electrochemical potentials involved. When electrons flow between the redox species, energy is produced [13].

Reactions occurring at the positive electrode (Fig. 1) are oxidation reactions during charging (anodic) and reduction reactions during discharging (cathodic). Similarly, reactions occurring at the negative electrode (Fig. 1) are reduction reactions during charging (cathodic) and oxidation reactions during discharging (anodic) [14].

The redox flow battery has a number of advantages over conventional rechargeable batteries such as the lead/acid or nickel/cadmium systems. As fully soluble redox couples and inert electrodes are used, undesirable electrode processes are eliminated (especially structural changes of the electrode). The system storage capacity is determined by the solution concentration and the size of the storage tanks, while the system power is determined by the number of individual cells

**Fig. 1** Schematic diagram of a redox flow energy storage system. Adapted from Ritchie and Siira [12] and Bartolozzi [18]



within a battery stack and their electrode area [8, 15]. As a result, it is possible to independently optimize the flow cell's storage capacity and the power output. Other attractive features of redox flow cells (as opposed to other electrochemical energy storage systems) are [10, 11]:

- simple electrode reactions;
- favorable exchange currents (for some redox couples);
- no requirement of high temperatures;
- no cycle life limitations (for the redox couples).

The only moving parts are the pumps, which need replacement every 5–7 years. One drawback of flow batteries, at least compared to other batteries, is their size. While the power cells are not extremely large, the storage tanks of electrolyte solution can be enormous [16]. Another concern is the toxicity of electrolytes employed. In addition, the redox flow battery has lower energy storage density in comparison to other electrochemical batteries. For these reasons, the technology is more attractive as a stationary storage device for load-leveling and stand-alone applications [17]. Various systems have been researched and developed with these applications in mind [18, 19] and these are reviewed in this paper. Some of the systems that have been considered are not strictly redox flow batteries, because their half-cell reactions involve the deposition of solid species. These systems have been clearly identified and are labeled as "hybrids". They are discussed here due to their similar design and operation to the redox flow battery.

The purpose of this paper is to highlight the major redox flow battery systems that have been designed and are undergoing development at present. Although similar work has already been published by the University of Southampton, [19], certain important types of flow batteries and redox species were omitted from that work (including the actinide redox species and the iron/titanium system). A general review was not attempted there and the focus was diverted toward system-operating conditions and charge/discharge characteristics of selected systems instead of an overall comparison of various technologies and their commercial potential. This paper attempts to discuss the technology in brief and can be considered as an extension to the original review of Bartolozzi [18]. Several new studies have also been published after that review paper [19] and have been considered in this work.

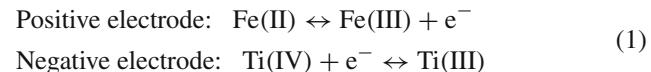
## 2 Common Redox Flow Systems Studied

### 2.1 Iron–Titanium Redox System

Thaller [11] discussed the possibility of employing a soluble Fe(III)/Fe(II)–Ti(IV)/Ti(III) redox system in aqueous hydrochloric acid solution for use in a redox flow battery.

Preliminary size and cost estimates for bulk energy storage using such redox couples were also evaluated [20]. It was found from these calculations that the size of a commercial redox flow battery system was <2 % of that of a comparable pumped hydroelectric plant. The overall costs of constructing such a system compared well with that of competing energy storage systems and savings in transmission costs were also achievable. However, the system was never commercialized due to the slow kinetics of the negative electrode reaction.

The charge/discharge reactions of the iron–titanium system are illustrated in Eq. 1 [21, 22].

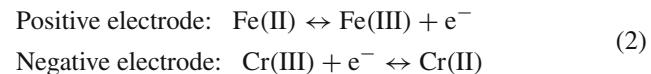


The open-circuit potential (OCP) of this system was 1.19 V while operating at room temperature, with an energy efficiency varying between 44 and 50 % [23, 24]. The energy density of the system was reported to be 13.25 Wh kg<sup>-1</sup>. These values were obtained for cells using lead as an electrocatalyst to enhance the kinetics of the titanium redox couple [Ti(IV)/Ti(III)] at a graphite negative electrode. The slow kinetics of this couple was also confirmed independently by other researchers [25]. Other workers [21] found that the kinetics of the titanium couple could be enhanced by impregnating the graphite negative electrode of their cell with palladium. However, further investigations using flow cells are yet to be carried out to compare their performance with the original prototype system developed by NASA [22].

### 2.2 Iron–Chromium Redox System

Many possible redox couples were screened by NASA [26, 27] since the first proposal of the redox flow cell concept by Thaller [11]. Out of several candidates for application as redox couples in the electrochemical energy storage system, the iron/chromium couple was selected and patented [11]. In general, the system consisted of acidified solutions of chromium [Cr(III)/Cr(II)] and iron [Fe(III)/Fe(II)], initially as unmixed reactants [8] and later as premixed solutions [28]. In premixed solutions, both the positive and negative electrolytes contained iron and chromium species as soluble salts in aqueous solutions of hydrochloric acid.

The charge and discharge processes for the iron–chromium system are illustrated in Eq. 2 [29].



The open-circuit potential of the system was 1.18 V at 29 °C. The highest energy efficiency of the system was approximately 73 % using premixed reactants [17] and an energy density of 15 Wh kg<sup>-1</sup> was also reported [15]. This was similar in magnitude to that of the iron–titanium system, if not better.



A 1 kW iron–chromium prototype redox flow battery was installed and tested in a photovoltaic system and its specifications are provided in Table 1 [30]. A schematic diagram of the system is shown in Fig. 2. Scale-up studies were also conducted by other workers [31–35] and these included the development of a 10 kW Fe–Cr redox battery prototype with an 80 % energy efficiency and 300 life cycles [36] and another 10 kW system involving the catholyte and anolyte circulation rates to save energy [37]. However, the system was not commercially developed due to problems of cross-contamination, membrane fouling [38,39] and the slow reaction of chromium redox species on most electrode surfaces [40]. Thus, this system was mainly ignored during the mid-1990s and early 2000s. In the late 2000s, however, the Fe–Cr battery was revisited by Deeya Energy in USA [41], when the world prices for vanadium briefly came close to four times its historical average prices and the company saw the Fe–Cr system as a potentially lower priced product than the all-vanadium redox flow battery.

### 2.3 Zinc–Bromine Hybrid Redox System

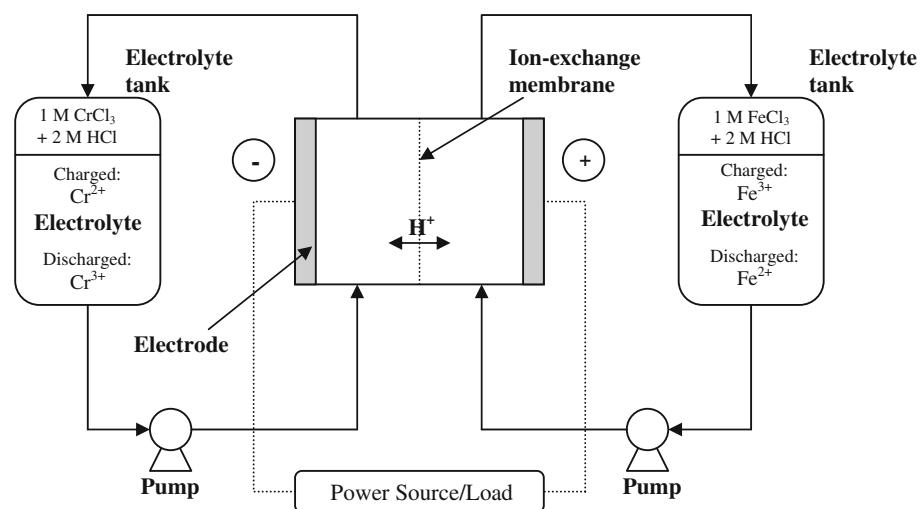
The zinc–bromine couple differs from a true redox flow system in that during the electrochemical conversion, zinc is

**Table 1** The system design parameters of a 1 kW prototype iron–chromium redox flow battery

Voltage (V)	120
Number of stacks	4
Number of cells per stack	39
Electrolyte volume (l)	700
Electrolyte energy density (Wh l <sup>-1</sup> )	14.5
Cell active area (cm <sup>2</sup> )	320
Current density (mA cm <sup>-2</sup> )	30
Electrolyte flow rate (cm <sup>3</sup> min <sup>-1</sup> )	100–150
Depth of discharge range (utilisation)	80–20 %

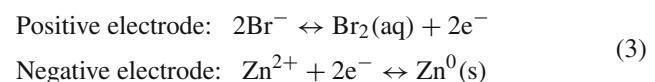
Adapted from Reid and Thaller [30]

**Fig. 2** A schematic diagram showing the general operation of an iron–chromium redox flow battery, adapted from Johnson and Reid [29] and Reid and Thaller [30]



plated onto one of the electrodes. However, it can be considered as a “hybrid” system and has thus been included in this paper. Nevertheless, the technology has many of the advantages of a true flow cell. The concept was first patented by Bradley as long ago as 1885 [4], but development of a commercial battery around that time was hindered by two factors: (1) the tendency of zinc to form dendrites upon deposition and (2) the high solubility of bromine in the aqueous zinc bromide electrolyte. Several successful attempts were made at overcoming these problems at Exxon and Gould in the mid-1970s and early 1980s [42,43], out of which one solution was the use of organic electrolytes such as propionitrile to reduce the bromine activity, thereby resulting in lower rates of self-discharge [44].

The charge/discharge reactions of the system are shown in Eq. 3 [43]:



The OCP of this system varies between 1.5 and 1.6 V at ambient temperature [43,45]. The zinc–bromine battery has had a few prototypes tested for both electric vehicles and energy storage applications [45]. The system, ranging in size from 50 to 400 kWh, is capable of storing energy for 2–10 h at efficiencies of 70 % or higher. Coulombic and voltage efficiencies were reported to be around 90 and 85 %, respectively, whereas the energy density was around 65–75 Wh kg<sup>-1</sup> [43]. Powercell of USA has developed a modularized system, based on a 100 kW zinc–bromine unit having a nominal 1 h discharge period. Several units can be coupled together to increase the power or energy storage rating. Units have been used in non-grid connected applications, for renewable energy storage as well as for distributed power generation [46,47].

The main advantages of this system include high energy density, high cell voltage, high degree of reversibility and

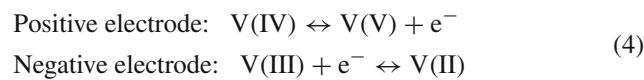


abundant, low cost reactants [46, 47]. The disadvantages of the Zn/Br<sub>2</sub> battery include high-cost electrodes, material corrosion, dendrite formation during zinc deposition on charge, high self-discharge rates, unsatisfactory energy efficiency and relatively low cycle life. In addition, the Zn/Zn<sup>2+</sup> couple reacts faster than the bromine/bromide couple causing polarization and eventually battery failure. To overcome this, high surface area carbon cathode is normally used, but this does not completely solve the problem [19]. Also bromine cross-over is still an important issue, as is the problem of dendritic growth and shorting. Electrolyte additives (e.g., quaternary ammonium salts) can be used to complex any dissolved bromine that has been inadvertently transported through the membrane to the zinc half-cell [47]. As a result, this system has been proposed for load leveling at the scale of 500 kWh, because of its low electrode polarization, low cost and wide availability of the active materials and electrodes.

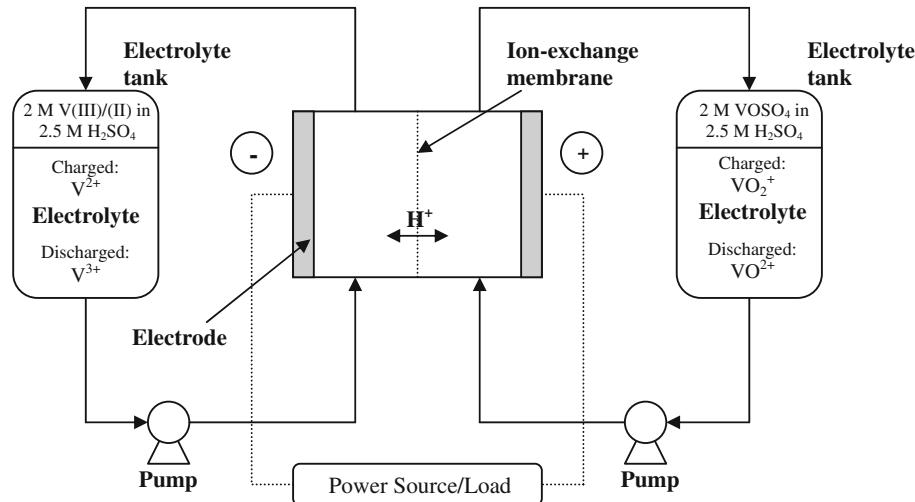
#### 2.4 All-Vanadium Redox System

The all-vanadium redox flow battery was first demonstrated in 1986 at the University of New South Wales (UNSW), Australia [48, 49]. The initial system developed at UNSW had an overall energy efficiency of 71 % and was patented [50]. Since then, further enhancements in the system were made until an overall efficiency of up to 90 % was achieved [5]. The OCP of this system was about 1.6 V and the energy density obtained was 25 Wh kg<sup>-1</sup> [51, 52]. The system has been operated over a temperature range of 15–40 °C successfully.

The charge/discharge reactions for the vanadium redox couples in aqueous sulfuric acid solutions are illustrated in Eq. 4 [53–55].



**Fig. 3** Schematic diagram showing the operation of the all-vanadium redox flow battery, adapted from Fabjan et al. [55] and Sumitomo [62]



Since 1993, a number of field trials were undertaken by the UNSW and other research organizations (such as Sumitomo, Japan). Among them, the vanadium redox flow battery system was evaluated in a solar demonstration house in Thailand [56] and with photovoltaic systems in Japan [57]. Both tests showed promising results in terms of high efficiencies and flexible operation. The system was also considered for submarine applications [58] as well as for electric vehicles [59]. Some details on a 1.5 MWh prototype battery for emergency backup power applications are given in Table 2. It is clear from Table 2 that the ion-exchange membrane accounted for approximately 51 % of the total capital cost of the system. A schematic diagram of the system is shown in Fig. 3.

An independent assessment of the charge/discharge performance of the vanadium redox flow battery was conducted in comparison to that of the lead–acid battery [60]. The net energy storage efficiency was greater for the vanadium system and it also had a lower environmental impact, justifying the considerable research into this technology that has been carried out. Additionally, the system has longer life (15 years) and greater range of discharge (see Table 3). Its components

**Table 2** Techno-economic details of a 1.5 MWh prototype vanadium redox flow battery for emergency backup power applications

Current density (A m <sup>-2</sup> )	500
Power density (kW m <sup>-2</sup> )	0.66
Electrode area (m <sup>2</sup> )	1.5
Area of graphite felt (m <sup>2</sup> )	3
Total cost of graphite felt (\$ kW <sup>-1</sup> )	315
Area of membrane (m <sup>2</sup> )	1.8
Cost of conducting plastic (\$ kW <sup>-1</sup> )	44
Total cost of membrane (\$ kW <sup>-1</sup> )	450
Cost of flow frames (\$ kW <sup>-1</sup> )	70
Total stack material cost (\$ kW <sup>-1</sup> )	879

Adapted from Skyllas-Kazacos and Menictas [58]



**Table 3** Comparison of performance of lead–acid battery as against a similar capacity vanadium redox flow battery [19, 52]

Lead–acid battery (in deep cycle)	Vanadium redox flow battery
Storage efficiency = 70–80 % approx.	Can reach 90 % or above
Storage capacity and power rating are interrelated through electrodes	Storage capacity and power rating can be optimized independently
Battery voltage can vary 10 % between charge and discharge states	Constant voltage during charging and discharging conditions
Significant damages caused by excessive charge and discharge	No life degradation from repeated deep discharge and recharge
Slow charging	Charging rate can vary to suit the given application
Damaged by rapid discharging	Can be discharged at any rate
Lifetime seriously reduced by rapid fluctuations in energy supply	Lifetime almost unaffected by rapid fluctuations in energy supply
Requires regular maintenance	Designed for unattended operation with very low maintenance costs
Lifetime rarely exceeds 5 years	Lifetime over 20 years between 20 and 80 % state-of-charge
Cross-contamination problems are common	Cross mixing of electrolytes does not lead to contamination of electrolyte
Self-discharge problems are common	Electrolyte remains fully charged, with low self-discharge, almost indefinitely
Environmental problems are likely from worn out systems	Proper engineering design ensures minimal environmental problems

are also highly recyclable and do not contribute toxic metals to the environment.

The application of a system for utility-scale electricity storage was also considered [61]. This vanadium redox flow battery was designed by Kashima-Kita (the biggest private electric company in Japan) to use vanadium compounds extracted from Orimulsion (emulsified natural asphalt with water, produced in Venezuela) as the electrolytes. An overall energy efficiency of 80 % was reported for a 200 kWh system.

Sumitomo Electric Industries Ltd., Japan, has built and tested several prototypes with capacities ranging from 170 to 1,000 kW with applications ranging from load leveling to photovoltaics. The response times of these prototypes have been estimated to be between 2 and 5 ms [62]. Further developments have taken place in Canada by VRB Power Systems Inc., which has acquired worldwide access to Sumitomo's patents and technology since 2005. The system has been used for applications from 2.5 kW to 10 MW with durations of 2 h and greater. All these developments show that by far, the vanadium redox flow battery has seen a greater amount of commercial success than other counterparts reviewed in this paper (with the exception of the zinc–bromine system).

There are currently two installations of the VRB-ESS (vanadium redox battery energy storage system) in commercial use:

1. Utah Power, a subsidiary of PacifiCorp, operates a VRB-ESS to meet the demands of a growing community in Castle Valley served by a 209-mile feeder system.
2. The second installation is in use by Hydro Tasmania on King Island, off the coast of Australia, to provide firm capacity from wind generators and optimize diesel generator performance.

Since 2002, several research groups have begun significant research and development activities on the VRB in China

and elsewhere [63]. These activities have expanded on the original work of Skyllas-Kazacos and co-workers and have covered the development of novel membranes, electrocatalysis, mechanistic studies of vanadium redox couples, cell modeling and simulation studies and stack development and demonstrations.

Despite the major advantages of the system, there exists the problem of a certain kind of vanadium ion V(V) that degrades the ion exchange membrane [19]. In addition, all-vanadium redox flow cells have a maximum vanadium concentration in the region of  $2 \text{ mol dm}^{-3}$ , which limits energy density and represents the solubility limit of V(II) and V(III) ions in sulfuric acid at temperatures from 5 up to 40 °C at which the V(V) ions are still stable [19]. In order to redress these issues, a novel redox flow battery was designed and investigated using the all-vanadium redox electrolytes [64]. The battery was cylindrical in shape and used carbon fibers with high specific surface area as electrodes and a porous silica glass with high chemical stability as the membrane material. Constant current charging–discharging tests showed that the batteries could deliver a specific energy of  $24 \text{ Wh L}^{-1}$  at a current density of  $55 \text{ mA cm}^{-2}$ . The open-circuit cell voltage, after full charging, remained constant at about 1.51 V for over 72 h, while the Coulombic efficiency was over 91 %, showing that there was negligible self-discharge due to active ions diffusing through the membrane during this period [64]. Other improvements include the use of Nafion/SiO<sub>2</sub> hybrid membrane to minimize cross-contamination [65] and the use of filter press-type reactors for achieving higher current densities [66].

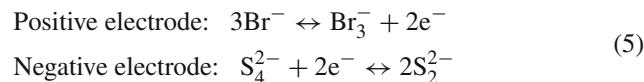
To realize the commercial potential of the all-vanadium RFB technology, a number of challenges must be overcome, notably scale-up and optimization (for example, with respect to flow geometries and operating conditions), improvement in electrolyte stability, development of electrode materials resistant to oxidation and mitigation of membrane degradation [67]. As a consequence, a number of mathematical



models have been developed to simulate the effect of oxygen and hydrogen evolution during the operation of the all-vanadium redox flow battery and measures to prevent gas production has also been suggested [67–69]. This proves that the technological development of this almost commercial technology is still in progress and further work is required for its full application in renewable energy storage.

## 2.5 Bromine/Polysulfide Redox System

Innogy Technology Ventures Limited had been developing a novel redox flow battery based on concentrated aqueous solutions of sodium bromide and sodium polysulfide since the early 1990s [70]. This technology was known as the Regenesys system. The nominal open-circuit cell voltage was 1.5 V and the cell energy efficiency was around 60–65 % depending on operating conditions. The cell operating temperature was between 20 and 40 °C. A schematic diagram illustrating the operation of the redox flow system is shown in Fig. 4. The charge/discharge reactions involved are shown in Eq. 5 [71]:



A fully charged sulfur–bromine redox flow battery mainly consisted of 1 mol dm<sup>-3</sup> flow-by sodium bromide solution saturated with bromine, in contact with a graphite electrode separated by a Nafion 125 ion exchange membrane from a 2 mol dm<sup>-3</sup> flow-through Na<sub>2</sub>S electrolyte, in contact with a porous sulfide nickel electrode [19, 70]. Other prototypes included nickel foam and carbon felt materials separated by a Nafion® 117 cationic membrane as negative and positive electrodes, respectively [66]. Both electrodes showed good electrocatalytic activity, but the internal ohmic resistance of the cell restricted the overall energy efficiency to 77.2 %, at a current density of 40 mA cm<sup>-2</sup> and cell power density

of 56 mW cm<sup>-2</sup>. A critical comparison between the performance of carbon felt electrodes against activated carbon was also made and it was determined that the former gave superior performance to the latter [72].

Challenges with this system included [19, 73]:

- cross-contamination problems of both electrolyte solutions over a period of time;
- difficulty in maintaining electrolyte balance;
- possibility of deposition of sulfur species in the membrane; and
- the need to prevent H<sub>2</sub>S(g) and Br<sub>2</sub>(g) formation.

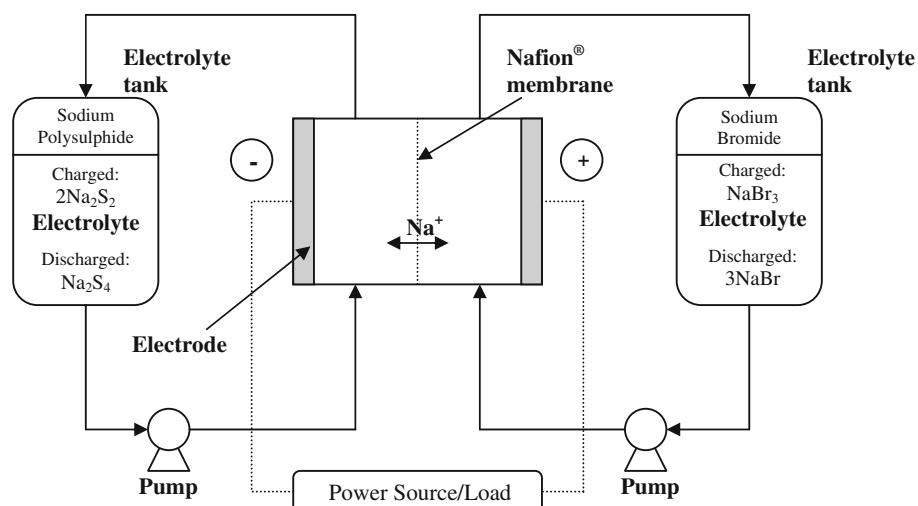
Despite these problems, a 1 MW system was successfully evaluated by Innogy back in [19]. In addition, Innogy Technology Ventures Limited started a project on a 15 MW/120 MWh utility-scale energy storage plant in August 2000 to be built alongside a 680 MW combined cycle gas turbine (CCGT) power station at Little Barford, Cambridgeshire [70]. Some plant parameters for the system are highlighted in Table 4.

Despite the apparent commercial success of this technology until 2002, Innogy was bought by a German firm (RWE AG) in 2003 and the Regenesys system was brought to a halt. The main reason behind this was that the Regenesys system had major problems due to poor sealing methods that resulted

**Table 4** Overall Regenesys® energy storage plant parameters—adapted from Innogy (2000)

Maximum rated power output (MW)	15
Energy storage capacity (MWh)	120
Discharge cycle (h)	6–14
Design availability (%)	95
Total number of modules	120
Predicted lifetime (years)	>15
Site area (m <sup>2</sup> )	<3,000

**Fig. 4** Schematic diagram showing the principle of operation of the Regenesys® redox flow battery. Adapted from Price et al. [71]



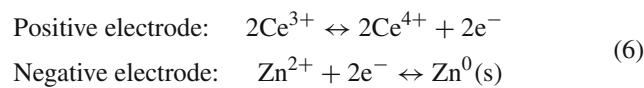
in electrolyte leaking and loss of cell efficiency. In addition to this problem, the cell stack was not straight, which resulted in further loss of electrolyte as well as efficiency. It was only a matter of time (late 2004) until VRB Power Systems Inc. (the firm involved in commercializing the vanadium redox flow battery in Canada) purchased an exclusive global license to the intellectual property and acquired all the related physical assets and inventory surrounding the Regenesys electricity storage technology.

Numerical modeling of the bromide polysulfide system revealed that mass transport overpotentials at the bromide electrode were found to limit the performance during discharge [74]. The model showed that significant drift in conditions could occur due to self-discharge and electro-osmotic effects. Careful electrolyte management was suggested to ensure reliable operation of the polysulfide–bromine (PSB) RFB system. A separate mathematical model incorporating capital and operating costs to predict the technical and commercial performance of PSB at a 120 MWh/15 MW utility-scale storage plant for arbitrage applications revealed a net loss of  $0.45 \text{ pkWh}^{-1}$  at an optimum current density of  $500 \text{ Am}^{-2}$  and an energy efficiency of 64 % [74]. Hence, plenty of research is still required to ensure that this system overcomes current techno-economic constraints in order to become a widespread commercialized technology.

## 2.6 The Hybrid Zinc–Cerium Redox System

A novel hybrid redox flow battery has been under development since the early 1990s by Electrochemical Design Associates Inc. The testing and development of this system has been contracted out to Plurion Systems Limited [19]. This system involves salts of zinc and cerium in an organic solvent as active electrolytes. It has some similarity to the zinc–bromine system in that the zinc redox couple involves a solid phase.

Due to the use of an environmentally benign organic acid as the solvent (not degraded by cross-membrane migration) and a common electrolyte system in both half-cells, the system has claimed a higher OCV than any of its commercial competitors. The charge/discharge reactions are shown in Eq. 6 [43, 64]:



The open-circuit voltage of the system is 2.4 V and it is claimed that the battery provides a superior power density than any other battery in the market [75]. So far, Plurion has developed scalable batteries with capacities ranging from 250–5,000 kW. A Zn/Ce system with a cell containing carbon plastic negative electrode and platinized titanium mesh

positive electrode of  $100 \text{ cm}^2$  geometrical area separated by a Nafion membrane was patented in 2004 [76].

The anolyte consisted of  $0.3 \text{ mol dm}^{-3}$   $\text{Ce}_2(\text{CO}_3)_3$  and  $1.3 \text{ mol dm}^{-3}$  of  $\text{ZnO}$  in 70 wt.% methanesulfonic acid at a flow rate of  $1.3\text{--}1.4 \text{ L min}^{-1}$ . The catholyte consisted of  $0.36 \text{ mol dm}^{-3}$   $\text{Ce}_2(\text{CO}_3)_3$  and  $0.9 \text{ mol dm}^{-3}$  of  $\text{ZnO}$  in 995 g of methanesulfonic acid at a flow rate of  $1.4\text{--}1.5 \text{ L min}^{-1}$ . The cell operating temperature was  $60^\circ\text{C}$  [19].

Mathematical modeling to understand the redox nature of the  $\text{Ce}(\text{IV})/\text{Ce}(\text{III})$  redox couple has also been conducted for a batch system comprising an electrochemical reactor and an electrolyte circuit [77]. The batch recycle system consisted of a pumped flow through divided FM01-LC parallel-plate electrochemical reactor ( $64 \text{ cm}^2$  projected electrode area) and a well-mixed tank ( $3,600 \text{ cm}^3$ ). In this work, significant differences between experimental and predicted values have been found at long electrolysis times. This is partly attributable to the presence of solvated species and complex formation involving  $\text{Ce}(\text{III})$  and  $\text{Ce}(\text{IV})$  species, which modify the actual concentration of  $\text{Ce}(\text{III})$  and  $\text{Ce}(\text{IV})$  together with the assumption of a simple, first-order reaction [77]. Additional investigation at the University of Southampton with a parallel-plate flow cell using three-dimensional electrodes revealed that the system performance improved at fast electrolyte velocities and at high temperatures of operation [78], yielding a maximum efficiency of 59.3 %. Also at reduced states of charge, it was possible to increase the number of charge/discharge cycles in the system. This was probably the first work that identified a significant limitation in the long-term operation of the system due to the zinc redox couple [78]. The main problem was due to the residues remaining on the zinc negative electrode after discharge [79]. A separate work by the same research group managed to extend the energy efficiency to 75 % at a charge/discharge current density of  $20 \text{ mA cm}^{-2}$  and at room temperature [79].

## 2.7 Soluble Lead–Acid Battery

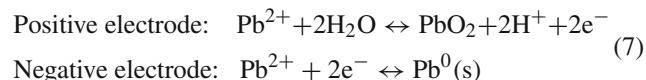
This system can be considered to be a breakthrough in the field of lead–acid battery technology. It has been included in this paper since the redox couples employed flow through the reactor system for charging and discharging purposes, similar to the redox flow battery.

The system differs from the traditional lead–acid battery as  $\text{Pb}(\text{II})$  is highly soluble in the aqueous acid electrolyte. It also differs from the reported redox flow batteries, because it only requires a single electrolyte, i.e., no separator or membrane is necessary; this reduces the cost and design complexity of the batteries significantly. The electrode reactions involve the conversion of the soluble species into a solid phase during charging and dissolution at the discharging cycles. This introduces complexities to the electrode reactions and might reduce the performance of the battery if the



metal growing across the interelectrode gap short circuits the battery. Dissolution and deposition of lead should be fast and no overpotential should be required; however, if overpotentials occur hydrogen evolution might take place thus reducing the storage capacity [80]. These cells have been studied in several electrolytes: perchloric acid, hydrochloric acid, hexafluorosilicic acid, tetrafluoroboric acid and most recently in methanesulfonic acid [80–84].

A schematic representation of a flowing undivided lead–acid battery is shown in Fig. 5. The charge/discharge reaction is shown in Eq. 7:



This system is still a new development and thus a number of issues remain unsolved regarding cost and technical performance. For instance, the electrode material is very expensive (reticulated vitreous carbon) due to which titanium mesh electrodes have also been investigated as an alternative. However, titanium may face problems due to passivation of the active surface and may limit the overall performance of the system [19]. Recent studies to improve system performance included addition of hexadecyltrimethylammonium cation,  $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$ , at a concentration of 5 mM [85], in-depth investigation of the  $\text{PbO}_2/\text{Pb}^{2+}$  couple in methanesulfonic acid [86] and extended cycling of the soluble lead–acid battery in a 10 cm  $\times$  10 cm parallel plate cell is possible [87]. It was found that extended cycling of the battery could lead to problems due to an imbalance in the Coulombic efficiency leading to deposits of Pb and  $\text{PbO}_2$  on the electrodes.

Extensive cycling of the soluble lead flow battery has revealed unexpected problems with the reduction of lead dioxide at the positive electrode during discharge [88]. This has led to a more detailed study of the  $\text{PbO}_2/\text{Pb}^{2+}$  couple in methanesulfonic acid. The variation of the phase composition measured by XRD and deposit structure measured

using SEM have been defined as a function of current density,  $\text{Pb}^{2+}$  and  $\text{H}^+$  concentrations, deposition charge and temperature as well as the consequences of charge cycling [88]. Pure  $\alpha$ - $\text{PbO}_2$ , pure  $\beta$ - $\text{PbO}_2$  and their mixtures can be deposited from methanesulfonic acid media successfully. The  $\alpha$ -phase deposits as a more compact, smoother layer, which is well suited to charge cycling. While the anodic deposition of thick layers of  $\text{PbO}_2$  is straightforward, their reduction is not; the complexities are explained by an increase in pH within the pores of the deposit. The results suggest that operating the battery at lead(II) concentrations  $<0.3$  M and elevated temperatures should be avoided [88]. Hence, more work is required before the system can be considered for commercialization projects.

## 2.8 Vanadium–Bromine Redox System

The vanadium–bromine redox flow battery has been under investigation for some time [89, 90]. The energy density is related to the concentration of the redox species in solution, on the cell potential and the number of electrons transferred during the discharge per mole of active redox ions [19]. The system employs the  $\text{VBr}_2/\text{VBr}_3$  redox couple at the negative electrode and the redox couple  $\text{Cl}^-/\text{BrCl}_2^-$  at the positive electrode as shown in Eq. 8 [19]:

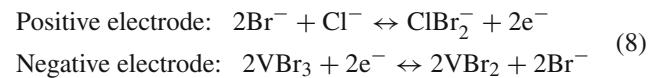
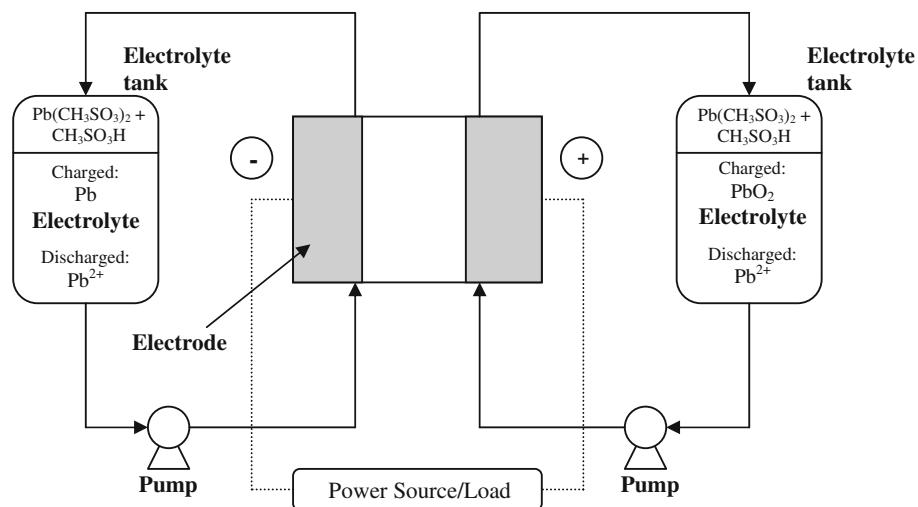
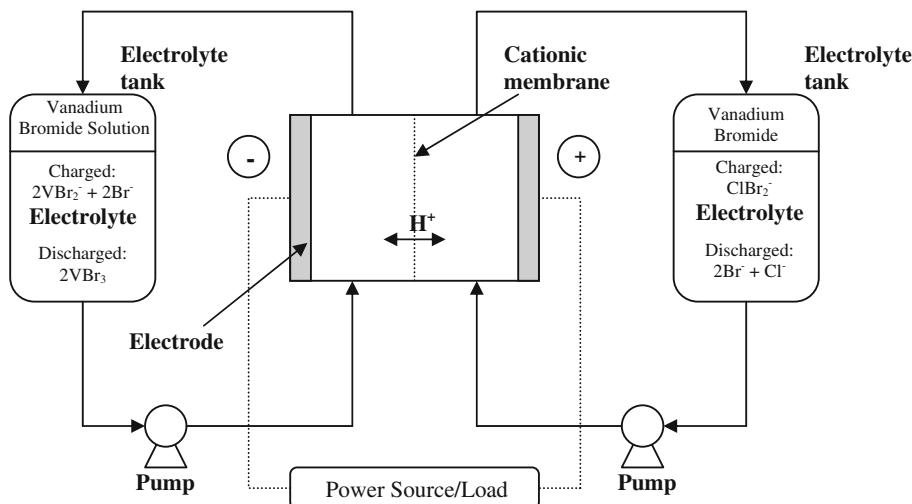


Figure 6 shows the principle behind the operation of the vanadium/bromine redox flow battery. Preliminary studies were carried out with this system using 3–4 mol  $\text{dm}^{-3}$  vanadium–bromide solution by Magnam Technologies [89]. For this concentration of active ions, it was possible to reach energy densities up to 50 Wh  $\text{kg}^{-1}$ . In addition, as the low solubility of the active vanadium species in the electrolyte of the all-vanadium redox battery limits its use to stationary

**Fig. 5** Schematic diagram showing the principle of operation of the soluble lead–acid battery. Adapted from Ponce de Leon et al. [19]



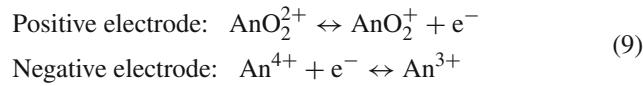
**Fig. 6** Schematic diagram showing the principle of operation of the vanadium–bromine redox flow battery. Adapted from Ponce de Leon et al. [19]



systems mainly, the vanadium–bromine system is being evaluated for possible applications in mobile systems such as electric buses and vans due to its higher energy density [91]. This system may be the new way forward for the all-vanadium redox flow battery system.

## 2.9 Actinide Redox Species

Actinide elements have also been proposed as active electrolytes for the redox flow battery [36, 92, 93]. The charge/discharge reactions for an all-actinide redox flow battery (redox species are represented by the abbreviation An) are shown in Eq. 9 [94]:



Two systems have been proposed as a means of utilizing excess depleted actinides for energy storage purposes. One involved the couples  $\text{Np}^{3+}/\text{Np}^{4+}$  and  $\text{NpO}_2^+/\text{NpO}_2^{2+}$  in aqueous solution [38], while the other considered the use of  $\text{U(IV)}/\text{U(III)}$  and  $\text{U(VI)}/\text{U(V)}$  couples in organic solvents [92–98]. An OCV of around 1 V was estimated for the all-uranium couples complexed by a range of  $\beta$ -diketone ligands [93]. Besides this, charge/discharge tests of the all-uranium redox flow battery has not been discussed significantly as yet. The same is the case for the all-neptunium redox couples, although theoretical calculations have revealed that an all-neptunium battery can produce energy efficiencies ranging from 40 to 99.1 % [94, 99]. 99.1 % efficiency is predicted at a current density of  $70 \text{ mA cm}^{-2}$ . The operation of a possible all-neptunium battery is shown in Fig. 7.

The use of radioactive redox species is likely to require special precautionary measures and a thorough investigation should be conducted to evaluate their safety and environmental implications before commercialization. For example, the high radioactivity of neptunium limited the practical

evaluation of the all-neptunium redox flow battery due to which only theoretical estimations of energy efficiencies are available [94].

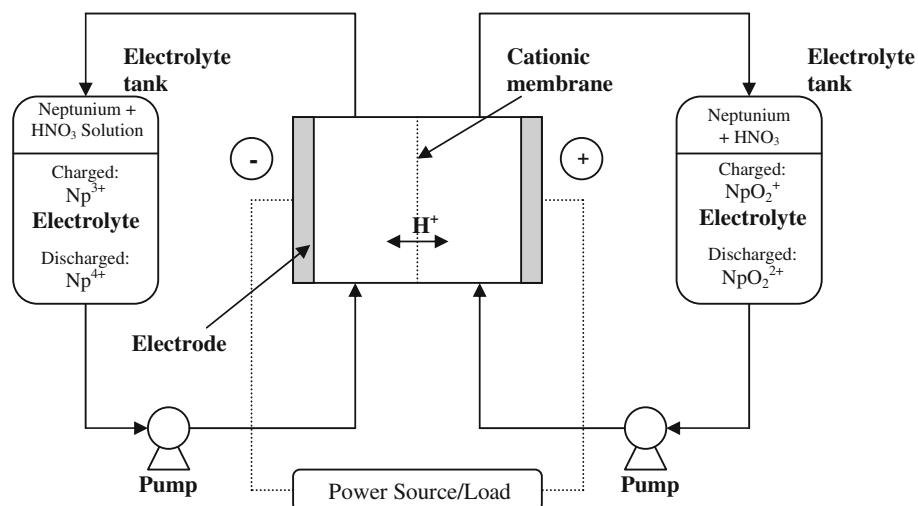
## 3 Novel Systems Tested Recently

Three independent research groups [39, 65, 100] have investigated the electrochemistry of the  $\text{Ce(IV)}/\text{Ce(III)}$  couple with the aim of coupling it with the  $\text{V(III)}/\text{V(II)}$  system to develop a new redox flow battery. Fang et al. [64] developed a laboratory-scale prototype redox flow battery that gave a higher OCV (1.9 V) than the all-vanadium system and an energy efficiency of around 68 %. In addition, cyclic voltammetric investigations have also confirmed the potential replacement of the  $\text{V(V)}/\text{V(IV)}$  couple with the  $\text{Ce(IV)}/\text{Ce(III)}$  couple [23]. However, scale-up studies are yet to be reported.

An all-chromium redox cell was investigated by Bae et al. [40], building on an original proposition made by Chen et al. [101]. The cell (static, H-type) employed chromium-EDTA complex as redox species in  $\text{HCl}$  media and energy efficiencies of 15 % was reported [40, 102]. Unfortunately, this redox species showed a poor performance when compared against the all-vanadium redox species, which was tested in a similar cell design [103]. Since then, the all-chromium species has not been considered for further evaluation in redox flow batteries. Studies with an undivided flow battery also revealed very low efficiency of 7 % for the aqueous all-chromium redox system [104]. Similarly, recent work with chromium acetylacetone complexes in acetonitrile gave low charge/discharge efficiencies in a stationary H-type glass cell [105] in a similar manner to the employment of vanadium acetylacetone in an earlier work [106]. Degradation mechanisms were later evaluated for the vanadium acetylacetone redox system suggesting that environmental oxygen and water were responsible for side reactions that lowered the efficiency of the H-type redox glass cell reactor [107].



**Fig. 7** Schematic diagram showing the principle of operation of the all-neptunium redox flow battery. Adapted from Yamamura et al. [92]



Organometallic redox species in acetonitrile solvent were proposed for redox flow batteries by Japanese researchers in the late 1980s [107, 108]. These species included tris(2,2'-bipyridine) ruthenium(II) tetrafluoroborate and ruthenium(III) acetylacetone. The former species was investigated in a redox flow cell, yielding an overall energy efficiency of 18 % [108]. The latter species was investigated by independent workers along with tris(2,2'-bipyridine) iron(II) perchlorate in a static H-type cell [102, 109, 110]. An energy efficiency of 74 % was reported for the ruthenium (III) acetylacetone species at 25 % state-of-charge. However, a slightly poorer performance was obtained when the same system was evaluated in an undivided redox flow battery reactor [107]. Other workers investigated manganese acetylacetone redox couples in acetonitrile in the H-type glass cell and obtained a meager energy efficiency of 21 % for an un-optimized system [111]. Results of the same system in a flow cell would be interesting.

The best temperature–concentration conditions for the vanadium–cerium RFB electrolytes appear to be 40 °C and 1 M sulfuric acid, where the relatively good solubility of both cerium species, the maximum values of redox potentials, and the more or less satisfying stability of glassy carbon electrodes were found [112]. Even so, the relatively low solubility of cerium salts in sulfuric acid media and slow redox kinetics of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox reaction at carbon indicate that the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  may not be well suited for use in RFB technology [112]. It is shown for the vanadium–cystine system that during charge, water transfer is significantly restricted with increasing concentration of HBr when the Nafion 115 cation exchange membrane is employed [113]. The same result can be obtained when the gas diffusion layer (GDL) hot-pressed separator is used. The organic electrosynthesis is directly correlated with the crossover of vanadium. When employing the anion exchange membrane, the electrosynthesis efficiency is over 96 % due to a minimal crossover of

vanadium. When the GDL hot-pressed separator is applied, the crossover of vanadium and water transfer are noticeably prevented and the electrosynthesis efficiency of over 99 % is obtained [113]. Those impurities such as vanadium ions and bromine can be eliminated through the purification of organic electrosynthesized products.

Performance of an RFB employing Mn(II)/Mn(III) couple as anolyte active species and V(III)/V(II) as catholyte ones was evaluated with constant-current charge–discharge tests [114]. The average Coulombic efficiency is 69.4 % and the voltage efficiency is 90.4 % at a current density of  $20 \text{ mA cm}^{-2}$ . The whole energy efficiency is 62.7 %, close to that of the all-vanadium battery and the average discharge voltage is about 14 % higher than that of an all-vanadium battery [114]. Although the results appear promising, further experimental studies are required in terms of durability of materials for long operations, shunt current losses and membrane fouling.

The zinc/nickel hybrid redox flow battery appears to give the highest energy efficiency of 86 % [115], followed by tiron/Pb redox flow battery in aqueous systems [116]. The zinc/nickel hybrid system does not require a membrane and thus its cost is likely to be less. However, the fact that the zinc half-cell involves electrodeposition of zinc on the active electrode is likely to limit the performance of the redox flow battery once scale-up studies are conducted. It is interesting to note that tiron (4,5-dibenzoquinone-1,3-benzenedisulfonate) was investigated in aqueous environment, whereas a similar aromatic species (rubrene) was investigated in organic media and gave very poor electrochemical conditions. It may be interesting to investigate tiron in organic media and compare its performance with that of the aqueous system to assess its suitability as active species in the positive electrolyte of an RFB [116]. On top of that, a preliminary understanding of its electrode mechanism in both acidic aqueous solutions and organic solvents may be attempted in an undivided



redox flow battery similar to the reactor reported by [117–120].

Methylimidazolium iron chlorides molten salt system has also been considered for redox flow battery applications [121]. For example, when sodium chloride/sodium (mp 1/4 7.88°C) electrode is combined with this EMICl–FeCl<sub>2</sub>–FeCl<sub>3</sub> molten salt, a high energy density per unit volume may be expected. Since Na(I)/Na couple in EMICl–AlCl<sub>3</sub> system has the formal potential of –2.15 V at room temperature [121], the electromotive force of approximately 2 V can be expected for the Na/EMICl–FeCl<sub>2</sub>–FeCl<sub>3</sub> battery. This battery may have the advantage of a low operation temperature and a long cycle life against Na–S and Zebra cells. On the other hand, the EMICl–FeCl<sub>2</sub>–FeCl<sub>3</sub> molten salt system itself is not necessarily suitable for the half-cell solution of the redox flow batteries presupposing the circulation of the half-cell solutions since the operation temperature must be higher than 110 °C. Thus, for this purpose, it is necessary to dilute the EMICl–FeCl<sub>2</sub>–FeCl<sub>3</sub> molten salt system with other room temperature ionic liquids or aprotic organic solvents [121]. Further work with this system appears to be lacking in the literature as focus has been more toward the all-vanadium and bromine/polysulfide systems over the years.

The electrochemical behavior of the Fe(III)/Fe(II)–triethanolamine (TEA) complex redox couple in alkaline medium and the influence of the concentration of TEA were investigated recently [122]. A change of the concentration of TEA mainly produces the following two results:

1. With an increase of the concentration of TEA, the solubility of the Fe(III)–TEA can be increased to 0.6 M, and the solubility of the Fe(II)–TEA is up to 0.4 M.
2. In high concentration of TEA with the ratio of TEA to NaOH ranging from 1 to 6, side reaction peaks on the cathodic main reaction of the Fe(III)–TEA complex at low scan rate can be minimized [122].

The electrode process of Fe(III)–TEA/Fe(II)–TEA is electrochemically reversible with higher reaction rate constant than the non-complexed species. Constant current charge–discharge shows that applying anodic active materials of relatively high concentrations facilitates the improvement of cell performance. The open-circuit potential of the Fe–TEA/Br<sub>2</sub> cell with the Fe(III)–TEA of 0.4 M, after full charging is nearly 2 V and is about 32 % higher than that of the all-vanadium batteries, together with the energy efficiency of approximately 70 % [122]. Further work on this system will highlight its potential for future commercialization or not.

#### 4 Miscellaneous Redox Couples Proposed for Future

A range of redox couples has been suggested and examined by various researchers and a few of these have also been

tested in redox flow batteries and chemically regenerative redox fuel cells [123]. Among those that underwent electrochemical scrutiny in *aqueous electrolytes* were: Fe(III)/Fe(II) complexes with a range of ligands [101, 124]; Co(III)/Co(II) complexes with various ligands [101]; Cr(III)/Cr(II); Br<sup>–</sup>/Br; Sn(II)/Sn(IV); Sb(III)/Sb(V); Cu(NH<sub>3</sub>)<sub>2</sub><sup>+1</sup>/Cu(NH<sub>3</sub>)<sub>4</sub><sup>+2</sup>; and Cr(CN)<sub>6</sub><sup>4–</sup>/Cr(CN)<sub>6</sub><sup>–3</sup> [27, 125]. Redox couples have also been investigated in *DMF*, including tris(2,2'-bipyridine) complexes of Cr(I)/Cr(II), Cr(II)/Cr(III), V(I)/V(0), V(0)/V(–I), V(–I)/V(–II), V(–II)/V(–III), Ti(0)/Ti(–I), Ti(–I)/Ti(–II), Mo(–I)/Mo(–II), and Mo(–II)/Mo(–III) [126]. Recently, a vanadium/oxygen flow battery has been reported to give efficiencies of 45.7 %, operating at a temperature of 80 °C [127]. The advantage of such a system is the lower weight and thus a greater weight-specific energy storage capacity than the conventional vanadium-based redox flow battery. However, the major obstacle in this system is the precipitation of vanadium ions from solution at room temperatures. As a result, further work is essential to overcome this problem so that this novel system can be operated without heating to save on costs.

In addition, aqueous and organic hybrid redox cells based on iron [18, 128] and zinc–ferricyanide [129] have been reported. However, no pilot-scale or commercial systems have been reported so far.

#### 5 Status of Commercialization

The two main systems that have come close to commercialization (all-vanadium and zinc–bromine) are reviewed briefly in this section. The technical issues involved in the commercialization of the iron–chromium and polysulfide–bromine systems have already been discussed in this paper earlier.

##### 5.1 All-Vanadium Redox Flow Battery

This system has had many practical demonstrations in the MW scale covering a wide range of applications in Japan, Europe and the USA [91, 130–133]. One of the main advantages of the vanadium redox flow battery includes its low cost for large storage capacities; cost per kWh decreases as energy storage capacity increases [134, 135].

In 1993, a consortium comprising Mitsubishi Chemicals and Kashima-Kita Power Corporation of Japan licensed the UNSW vanadium battery technology for stationary uses and has since spent several million dollars each year to scale up the technology for large-scale load-leveling and solar energy storage applications [46, 134]. Kashima-Kita Electric Power Corporation employs vanadium-rich Venezuelan pitch as the fuel for electricity generation, thus producing a high vanadium content fly ash as a waste product. A 3 m<sup>3</sup> d<sup>–1</sup> electrolyte production plant has been commissioned in 1996 [46, 134, 135].



In 1999, license rights to the original UNSW all-vanadium battery technology were acquired by Sumitomo Electric Industries (SEI) in Japan. SEI subsequently completed more than 20 medium to large VRB demonstration systems in a wide range of applications, including wind energy storage, emergency back-up power and load leveling, demonstrating overall energy efficiencies as high as 80 % and up to 270,000 charge–discharge cycles [136].

In 2001, a vanadium energy storage system (VESS) incorporating a 250 kW/520 kWh vanadium redox battery was established in South Africa and it was its first large-scale commercial trial of user-based applications [135]. Pinnacle VRB installed 250 kW/1 MWh system for Hydro Tasmania in Australia for wind energy storage and the replacement of diesel fuel in 2003 [46, 134, 135], while VRB power installed a 250 kW/2 MWh system in the USA for voltage support and rural feeder augmentation in 2004 [46, 134]. In addition, SEI in Japan installed a 4 MW/6 MWh system at Subaru Wind Farm for wind energy storage and power stabilization in 2005 [66]. The latter system was reported to give overall round trip energy efficiency of 80 % with cycle life of over 270,000 cycles over 3 years of testing [136].

In 2001, the early UNSW patents were acquired by the Canadian company VRB Power and then by Prudent Energy in China where significant commercialization took place [135]. Early VRB stack development in China was initiated using a 1 kW vanadium battery stack that was designed and tested in 2006. Coulombic, voltage and energy efficiencies of 85.9, 91.1 and 78.3 %, respectively, were obtained at a current density of  $60 \text{ mA cm}^{-2}$ , with a maximum average output power of 1.35 kW at a discharge current density of  $85 \text{ mA cm}^{-2}$  [135]. The 1 kW modules were subsequently integrated into a 10 kW battery with a series by parallel configuration of  $4 \times 2$  and an overall energy efficiency of more than 80 % was obtained at an average output power of 10.05 kW (current density  $85 \text{ mA cm}^{-2}$ ) [136].

In July 2009, Chinese National Grid announced the launch of the Zhangbei storage building, China's first comprehensive demonstration project, which included an energy storage project ranging in size to about 75 MW. Technologies such as all-vanadium, lithium-ion and the Japanese Sumitomo sodium sulfur batteries were included in several demonstration projects for energy storage. However, for wind energy storage, the all-vanadium redox battery was found to be most desirable [136].

In 2010, the US Department of Energy funded the demonstration of a 1 MW/8 MWh vanadium redox battery for load leveling trials at the Painesville Municipal Power Station in Ohio [135] and this project includes the development of 10–20 kW stacks for mass production. Other developments are underway in China and have been reported in detail in another review [136].

## 5.2 Zinc–Bromine Flow Battery

A couple of projects were undertaken by ZBB Energy Corporation to evaluate the ability of the zinc–bromine system for solar energy storage [135]. In the first project, a 50 kW rooftop PV (photovoltaic) system was installed in parallel with a 50 kW/100 kWh battery system at a commercial facility in New York. The second project was a 250 kW/500 kWh utility system that was installed on a remote utility circuit in New South Wales, Australia. This system was meant to complement an existing 20 kW PV concentrator system, support the remote line and offer enhanced reliability. The battery was charged by the solar array during the day in order to provide reliable nighttime power to remote area property owners [136].

Two other companies that are currently commercializing the zinc–bromine battery are Premium Power based in Massachusetts [137] and Redflow based in Queensland Australia [138] which have modular units that deliver up to 500 and 30 kWh of electricity storage, respectively. The systems are designed as integrated power generation units complete with inverters and power conditioning equipment within a transportable trailer for easy installation. Despite such major developments, further scale-up and full commercialization of the zinc–bromine technology are yet to become a reality possibly due to problems related to zinc deposition at the cathode during charge that can lead to dendrites and short-circuiting across the separator [136].

## 6 Conclusions

Various redox flow battery systems have been developed and investigated to enhance the performance of secondary battery energy storage technology. Most systems reported in this paper used an aqueous solvent and as a result their open circuit potentials (an indication of the energy storage capacity) were limited by the water electrolysis reaction. Some hybrid systems have also been reported that employed organic solvents, thereby overcoming this problem. However, the capital cost of the system was high due to the use of an expensive ion-exchange membrane to separate charged electrolytes. In addition, the membrane also resulted in cycle life limitations and energy losses due to fouling and cross-migration of charged species.

Other technical issues limiting the commercialization of the redox flow battery were discussed in detail by Ponce de Leon et al. [19]. Despite the advances made by VRB Power Systems Inc. and other organizations (such as Sumitomo), further research is necessary to ensure that redox flow batteries gain a widespread commercial advantage over and above other means of large-scale energy storage technologies. One possible area of research is in improving the quality of the ion-exchange membrane to reduce the problems from



cross-contamination and membrane fouling. Other configurations may need to be investigated into, such as incorporation of porous electrodes, organo-metallic redox species with fast electrochemical kinetics (to provide a higher energy capacity), chemical additives (such as nanoplatelets for improving electrochemical kinetics of redox species [139]) and others. The performance of redox flow cells indicated by the volumetric energy density (in  $\text{kWh m}^{-3}$ ) can be enhanced by means of porous, three-dimensional electrodes, highly catalytic electrodes, high linear velocities and good turbulence promoters [120]. Further work is also required in the areas of [19, 119, 136]:

- (a) reactor characterization,
- (b) catalysis by composite (carbon-polymer) electrodes,
- (c) membrane performance,
- (d) membrane-free systems,
- (e) large-scale engineering of redox flow cell systems and their integration with other energy systems,
- (f) porous flow-through and flow-by electrodes, and
- (g) organic redox couples.

Clearly, this field is open for further research and development in order to produce economical redox flow batteries for widespread commercial applications. So far, it is practical to surge ahead with the vanadium–bromine redox flow battery in conjunction with the bromine–polysulfide system until and unless suitable alternatives are found that can help in eliminating the ion-exchange membrane altogether.

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## References

1. Cassidy, E.S.; Grossman, P.Z.: *Introduction to Energy-Resources, Technology and Society*, 2nd edn. Cambridge University Press, Cambridge (2000)
2. Brown, A.: *The UK New and Renewable Energy Programme. Investment in Renewable Energy Professional Engineering Publishing Limited*, IMechE, UK (1998)
3. Wolsky, A.M.: The status and prospects for flywheels and SMES that incorporate HTS. *Phys. C* **372–376**, 1495–1499 (2002)
4. Jensen, J.: *Energy Storage*. Newnes-Butterworths, London (1980)
5. Skyllas-Kazacos, M.; Kasherman, D.; Hong, D.R.; Kazacos, M.: Characteristics and performance of 1 kW UNSW vanadium redox battery. *J. Power Sources* **35**, 399–404 (1991)
6. Baker, J.N.; Collinson, A.: Electrical energy storage at the turn of the Millennium. *Power Eng. J.* **13**, 107–112 (1999)
7. Xu, Y.; Wen, Y.; Cheng, J.; Cao, G.; Yang, Y.: Study on a single flow acid Cd–chloranil battery. *Electrochem. Commun.* **11**, 1422–1424 (2009)
8. Thaller, L.H.: Redox Flow Cell Energy Storage Systems. NASA TM-79143, USA (1979)
9. Hurwitch, J.W.: Opportunities for Advanced Battery Storage in Competitive Electric Market. *Energy Storage Technologies for Utility Network Optimisation*, EA Technology, Capenhurst (1996)
10. Hajimolana, S.A.; Soroush, M.: Dynamics and Control of a Tubular Solid-Oxide Fuel Cell. *Ind. Eng. Chem.* **48**, 6112–6125 (2009)
11. Thaller, L.H.: Electrically rechargeable redox flow cells. In: *Proceedings of the 9th IECEC Meeting*, San Diego, California, USA (1974)
12. Ritchie, I.M.; Siira, O.T.: Redox batteries—an overview. In: *8th Biennial Congress of International Solar Energy*, Perth, Australia (1983)
13. Skyllas-Kazacos, M.; Grossmith, F.: Efficient vanadium redox flow cell. *J. Electrochem. Soc.* **134**, 2950–2953 (1987)
14. Vincent, C.A.; Bonino, F.; Lazzari, M.; Scrosati, B.: *Modern Batteries an Introduction to electrochemical power sources*. Edward Arnold, London (1984)
15. Rychcik, M.; Skyllas-Kazacos, M.: Characteristics of a new all-vanadium redox flow battery. *J. Power Sources* **22**, 59–67 (1988)
16. Li, X.G.; Huang, K.L.; Liu, S.Q.; Tan, N.; Chen, L.Q.: Characteristics of graphite felt electrode electrochemically oxidized for vanadium redox battery application. *Trans. Nonferrous Metals Soc. China* **17**, 195–199 (2007)
17. Lopez-Atalaya, M.; Codina, G.; Perez, J.R.; Vazquez, J.L.; Aldaz, A.: Optimization studies on a Fe/Cr redox flow battery. *J. Power Sources* **39**, 147–154 (1992)
18. Bartolozzi, M.: Development of redox flow batteries. A historical bibliography. *J. Power Sources* **27**, 219–234 (1989)
19. Ponce De Leon, C.; Frias-Ferrer, A.; Gonzalez-Garcia, J.; Szanto, D.A.; Walsh, F.C.: Redox flow cells for energy conversion. *J. Power Sources* **160**, 716–732 (2006)
20. Warshay, M.; Wright, L.O.: Cost and size estimates for a redox bulk energy storage concept. *J. Electrochem. Soc.* **124**, 173–177 (1977)
21. Wang, Y.Y.; Lin, M.R.; Wan, C.C.: A study of the discharge performance of the Ti/Fe redox flow system. *J. Power Sources* **13**, 65–74 (1984)
22. Savinell, R.F.; Liu, C.C.; Galasco, R.T.; Chiang, S.H.; Coetze, J.F.: Discharge characteristics of a soluble iron–titanium battery system. *J. Electrochem. Soc.* **126**, 357–360 (1979)
23. Liu, C.C.; Galasco, R.T.; Savinell, R.F.: Enhancing performance of the Ti(III)/Ti(IV) couple for redox battery applications. *J. Electrochem. Soc.* **128**, 1755–1757 (1981)
24. Liu, C.C.; Galasco, R.T.; Savinell, R.F.: Operating performance of an Fe–Ti stationary redox battery in the presence of lead. *J. Electrochem. Soc.* **129**, 2502–2505 (1982)
25. Mariani, M.P.; Bartolozzi, M.; Moncelli, M.R.: Determination of the kinetic parameters for the Ti(III)/Ti(IV) couple using a rotating disk electrode. *J. Electroanal. Chem.* **209**, 275–282 (1986)
26. Giner, J.; Cahill, K.: Advanced Screening of Electrode Couples. NASA CR-159738, USA (1980)
27. Giner, J.; Swette, L.; Cahill, K.: Screening of Redox Couples and Electrode Materials. Giner, Inc., Waltham, Massachusetts, Contract report for NASA, Lewis Research Centre, NASA-19760, USA (1976)
28. Gahn, R.F.H.; Hagedorn, N.H.; Johnson, J.A.: Cycling performance of the iron–chromium redox energy storage system. NASA TM-87034, Department of Energy, USA (1985)
29. Johnson, D.A.; Reid, M.A.: Chemical and electrochemical behaviour of the Cr(III)/Cr(II) half-cell in the iron–chromium redox energy storage system. *J. Electrochem. Soc.* **132**, 1058–1062 (1985)



30. Reid, M.A.; Thaller, L.H.: Preparation and characterization of electrodes for the NASA redox storage system. NASA TM-82702, USA (1980)

31. Fedkiw, P.S.W.; Watts, R.W.: A mathematical model for the iron/chromium redox battery. *J. Electrochem. Soc.* **131**, 701–709 (1984)

32. Takahashi, S.; Hiramatsu, T.: Overview of rechargeable battery testing in Japan. *J. Power Sources* **17**, 55–63 (1986)

33. Futamata, M.; Higuchi, S.; Nakamura, O.; Ogino, I.; Takada, Y.; Okazaki, S.: Performance testing of 10 kW-class advanced batteries for electric energy storage systems in Japan. *J. Power Sources* **24**, 137–155 (1988)

34. Codina, G.; Perez, J.R.; Lopez-Atalaya, M.; Vasquez, J.L.; Aldaz, A.: Development of a 0.1 kW power accumulation pilot plant based on an Fe/Cr redox flow battery Part I. Considerations on flow-distribution design. *J. Power Sources* **48**, 293–302 (1994)

35. Codina, G.; Aldaz, A.: Scale-up studies of an Fe/Cr redox flow battery based on shunt current analysis. *J. Appl. Electrochem.* **22**, 668–674 (1992)

36. Shimizu, M.; Mori, N.; Kuno, M.; Mizunami, K.; Shigematsu, T.: Development of a redox flow battery. *Proc. Electrochem. Soc.* **88-11**, 249–256 (1988)

37. Nakamura, Y.: Japanese Patent. 63150863 (1988)

38. Shiokawa, Y.; Yamana, H.; Moriyama, H.: An application of actinide elements for a redox flow battery. *Nuclear Sci. Tech.* **37**, 253–256 (2000)

39. Paulenova, A.; Creager, S.E.; Navratil, J.D.; Wei, Y.: Redox potentials and kinetics of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  redox reaction and solubility of cerium sulfates in sulfuric acid solutions. *J. Power Sources* **109**, 431–438 (2002)

40. Bae, C.H.; Roberts, E.P.L.; Dryfe, R.A.W.: Chromium redox couples for application to redox flow batteries. *Electrochim. Acta* **48**, 279–287

41. Deeya Energy website. <http://www.deeyaenergy.com/product/>. Accessed 29-5-2011

42. Butler, P.C.; Miller, D.W.; Verardo, A.E.: Flowing electrolyte battery testing and evaluation. In: Proceedings of the 17th IECEC Meeting, pp. 653–658 (1982)

43. Butler, P.C.; Eidler, P.A.; Grimes, P.G.; Klassen, S.E.; Miles, R.C.: Zinc/Bromine Batteries. *Handbook of Batteries*, 2nd edn. McGraw-Hill Inc., New York (1995)

44. Singh, P.; White, K.; Parker, A.J.: Application of non-aqueous solvents to batteries—part I. Physicochemical properties of propionitrile-water two-phase solvent relevant to zinc–bromine batteries. *J. Power Sources* **10**, 309–318 (1983)

45. Lex, P.; Jonshagen, B.: The zinc/bromine battery system for utility and remote area applications. *Power Eng. J.* **13**, 142–148 (1999)

46. Skyllas-Kazacos, M.: Secondary Batteries: Redox Flow Battery–Vanadium Redox. *Encyclopedia of Electrochemical Power Sources*, Elsevier, Amsterdam (2009)

47. Watt-Smith, M.J.; Wills, R.G.A.; Walsh, F.C.: Secondary batteries—flow systems. *Encyclopedia of Electrochemical Power Sources*. Elsevier, Amsterdam (2010)

48. Skyllas-Kazacos, M.; Rychcik, M.; Robins, R.; Fane, A.; Green, M.: New all-vanadium redox flow cell. *J. Electrochem. Soc.* **133**, 1057–1058 (1986)

49. Rychcik, M.; Skyllas-Kazacos, M.: Evaluation of electrode materials for vanadium redox cell. *J. Power Sources* **19**, 45–54 (1987)

50. Skyllas-Kazacos, M.; Robins, R.: All-vanadium redox battery. US Patent 4,786,567 (1988)

51. Skyllas-Kazacos, M.; Peng, C.; Cheng, M.: Evaluation of precipitation inhibitors for supersaturated vanadyl electrolytes for the vanadium redox battery. *electrochem solid state let* **2**, 121–122 (1999)

52. Williams, B.R.; Hennessy, T.: Electric oasis. *IEE Power Eng.* **19**, 28–31 (2005)

53. Sum, E.; Rychcik, M.; Skyllas-Kazacos, M.: Investigation of the  $\text{V(V)}/\text{V(IV)}$  system for use in the positive half-cell of a redox battery. *J. Power Sources* **16**, 85–95 (1985)

54. Sum, E.; Skyllas-Kazacos, M.: A study of the  $\text{V(II)}/\text{V(III)}$  redox couple for redox flow cell applications. *J. Power Sources* **15**, 179–190 (1985)

55. Fabjan, C.; Garche, J.; Harrer, B.; Jorissen, L.; Kolbeck, C.; Philipp, F.: The vanadium redox-battery: an efficient storage unit for photovoltaic systems. *Electrochim. Acta* **47**, 825–831 (2001)

56. Menictas, C.; Cheng, M.; Skyllas-Kazacos, M.: Evaluation of  $\text{NH}_4\text{VO}_3$  derived electrolyte for vanadium redox flow battery. *J. Power Sources* **45**, 43–54 (1993)

57. Tsuda, I.; Nozaki, K.; Sakata, K.; Kurokawa, K.: Improvement of performance in redox flow batteries for PV systems. *Solar Energy Material Solar Cells* **47**, 101–107 (1997)

58. Skyllas-Kazacos, M.; Menictas, C.: The vanadium redox battery for emergency back-up applications. In: *Proceedings of Intelec 97 Melbourne*, pp. 19–23 (1997)

59. Rand, D.A.J.; Woods, R.; Dell, R.M.: *Batteries for electric vehicles*. Wiley, New York (1998)

60. Rydh, C.J.: Environmental assessment of vanadium redox and lead–acid batteries for stationary energy storage. *J. Power Sources* **80**, 21–29 (1999)

61. Shibata, A.; Sato, K.: Development of vanadium redox flow battery for electricity storage. *Power Eng. J.* **13**, 130–135 (1999)

62. Sumitomo Electric Industries. *Vanadium Redox Flow Battery*. <http://global-sei.com/>. Accessed 28-05-2011

63. Huang, K.L.; Li, X.G.; Liu, S.Q.; Tan, N.; Chen, L.Q.: Research progress of vanadium redox flow battery for energy storage in China. *Renew. Energy* **33**, 186–192 (2008)

64. Fang, B.; Iwasa, S.; Wei, Y.; Arai, T.; Kumagai, M.: Study of the  $\text{Ce(III)}/\text{Ce(IV)}$  redox couple for redox flow battery application. *Electrochim. Acta* **47**, 3971–3976 (2002)

65. Xi, J.; Wu, Z.; Qiu, X.; Chen, L.: Nafion/SiO<sub>2</sub> hybrid membrane for vanadium redox flow battery. *J. Power Sources* **166**, 531–536 (2007)

66. Zhao, P.; Zhang, H.; Zhou, H.; Yi, B.: Nickel foam and carbon felt applications for sodium polysulfide/bromine redox flow battery electrodes. *Electrochim. Acta* **51**, 1091–1098 (2005)

67. Al-Fetlawi, H.; Shah, A.A.; Walsh, F.C.: Non-isothermal modelling of the all-vanadium redox flow battery. *Electrochim. Acta* **55**, 78–89 (2009)

68. Al-Fetlawi, H.; Shah, A.A.; Walsh, F.C.: Modelling the effects of oxygen evolution in the all-vanadium redox flow battery. *Electrochim. Acta* **55**, 3192–3205 (2009)

69. Shah, A.A.; Al-Fetlawi, H.; Walsh, F.C.: Dynamic modelling of hydrogen evolution effects in the all-vanadium redox flow battery. *Electrochim. Acta* **55**, 1125–1139 (2010)

70. Walsh, F.C.: Electrochemical technology for environmental treatment and clean energy conversion. *Pure Appl. Chem.* **73**, 1819–1837 (2001)

71. Price, A.; Bartley, S.; Male, S.; Cooley, G.: A novel approach to utility scale energy storage. *Power Eng. J.* **13**, 122–129 (1999)

72. Zhao, P.; Zhang, H.; Zhou, H.; Chen, J.; Gao, S.; Yi, B.: Characteristics and performance of 10kW class all-vanadium redox-flow battery stack. *J. Power Sources* **162**, 1416–1420 (2006)

73. Licht, S.; Davis, J.: Disproportionation of aqueous sulphur and sulphide: kinetics of polysulphide decomposition. *J. Phys. Chem.* **101**, 2540–2545 (1997)

74. Scamman, D.P.; Reade, G.W.; Roberts, E.P.L.: Numerical modelling of a bromide-polysulphide redox flow battery. Part 2: evaluation of a utility-scale system. *J. Power Sources* **189**, 1231–1239 (2009)

75. Scamman, D.P.; Reade, G.W.; Roberts, E.P.L.: Numerical modelling of a bromide-polysulphide redox flow battery. Part 1:



modelling approach and validation for a pilot-scale system. *J. Power Sources* **189**, 1220–1230 (2009)

76. Clarke, R.; Dougherty, B.; Mohanta, S.; Harrison, P.: Cerium-zinc regenerative fuel cell. In: Joint International Meeting-206th Meeting of the Electrochemical Society/2004 Fall Meeting of the Electrochemical Society of Japan, Honolulu, HI, pp. 1–520 (2004)

77. Trinidad, P.; Ponce-de-Leon, C.; Walsh, F.C.: The use of electrolyte redox potential to monitor the Ce(IV)/Ce(III) couple. *J. Environ. Manage.* **88**, 1417–1425 (2008)

78. Leung, P.K.; Ponce-de-Leon, C.; Low, C.T.J.; Shah, A.A.; Walsh, F.C.: Characterization of a zinc–cerium flow battery. *J. Power Sources* **196**, 5174–5185 (2011)

79. Leung, P.K.; Ponce-de-Leon, C.; Walsh, F.C.: An undivided zinc–cerium redox flow battery operating at room temperature (295 K). *Electrochem. Commun.* **13**, 770–773 (2011)

80. Pletcher, D.; Wills, R.: A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II). Part II. Flow cell studies. *Phys. Chem. Chem. Phys.* **6**, 1779–1785 (2004)

81. Ponce-de-Leon, C.; Reade, G.W.; Whyte, I.; Male, S.E.; Walsh, F.C.: Characterization of the reaction environment in a filter-press redox flow reactor. *Electrochim. Acta* **52**, 5815–5823 (2007)

82. Pletcher, D.; Wills, R.: A novel flow battery—a lead acid battery based on an electrolyte with soluble lead(II): III. The influence of conditions on battery performance. *J. Power Sources* **149**, 96–102 (2005)

83. Hazza, A.; Pletcher, D.; Wills, R.: A novel flow battery—a lead acid battery based on an electrolyte with soluble lead(II): Part I. Preliminary studies. *Phys. Chem. Chem. Phys.* **6**, 1773–1778 (2004)

84. Hazza, A.; Pletcher, D.; Wills, R.: A novel flow battery—a lead acid battery based on an electrolyte with soluble lead(II): IV. The influence of additives. *J. Power Sources* **149**, 103–111 (2005)

85. Pletcher, D.; Zhou, H.; Kear, G.; Low, C.T.J.; Walsh, F.C.; Wills, R.G.: A novel flow battery—a lead–acid battery based on an electrolyte with soluble lead(II): Part VI. Studies of the lead dioxide positive electrode. *J. Power Sources* **180**, 630–634 (2008)

86. Li, X.; Pletcher, D.; Walsh, F.C.: A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): Part VII. Further studies of the lead dioxide positive electrode. *Electrochim. Acta* **54**, 4688–4695 (2009)

87. Collins, G.; Kear, X.L.; Low, C.T.J.; Pletcher, D.; Tangirala, R.; Stratton-Campbell, D.; Walsh, F.C.; Zhang, C.: A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II) Part VIII. The cycling of a 10 cm × 10 cm flow cell. *J. Power Sources* **195**, 1731–1738 (2010)

88. Li, X.; Pletcher, D.; Walsh, F.C.: A novel flow battery: a lead acid battery based on an electrolyte with soluble lead(II): Part VII. Further studies of the lead dioxide positive electrode. *Electrochim. Acta* **2009**, 4688–4695 (2009)

89. Skyllas-Kazacos, M.: Novel vanadium chloride/polyhalide redox flow battery. *J. Power Sources* **124**, 299–302 (2003)

90. Skyllas-Kazacos, M.; Limantari, Y.: Kinetics of the chemical dissolution of vanadium pentoxide in acidic bromide solutions. *J. Appl. Electrochem.* **34**, 681–685 (2004)

91. Skyllas-Kazacos, M.; Kazacos, G.; Poon, G.; Verseema, H.: Recent advances with UNSW vanadium-based redox flow batteries. *Int. J. Energy Res.* **34**, 182–189 (2010)

92. Yamamura, T.; Shiokawa, Y.; Ikeda, Y.; Tomiyasu, H.: Electrochemical investigation of tetravalent uranium beta-diketones for active materials of all-uranium redox flow battery. *Nuclear Sci. Tech.* **3**, 445–448 (2002)

93. Yamamura, T.; Shiokawa, Y.; Yamana, H.; Moriyama, H.: Electrochemical investigation of uranium [beta]-diketonates for all-uranium redox flow battery. *Electrochim. Acta* **48**, 43–50 (2002)

94. Yamamura, T.; Shirasaki, K.; Li, D.X.; Shiokawa, Y.: Electrochemical and spectroscopic investigations of uranium(III) with N,N,N',N'-tetramethylmalonamide in DMF. *J. Alloys Comp.* **418**, 139–144 (2006)

95. Yamamura, T.; Shirasaki, K.; Shiokawa, Y.; Nakamura, Y.; Kim, S.Y.: Characterization of tetraketone ligands for active materials of all-uranium redox flow battery. *J. Alloys Comp.* **374**, 349–353 (2004)

96. Yamamura, T.; Watanabe, N.; Shiokawa, Y.: Characterization of tetraketone ligands for active materials of all-uranium redox flow battery. *J. Alloys Comp.* **408**, 1260–1266 (2006)

97. Shirasaki, K.; Yamamura, T.; Herai, T.; Shiokawa, Y.: Electrodeposition of uranium in dimethyl sulfoxide and its inhibition by acetylacetone as studied by EQCM. *J. Alloys Comp.* **418**, 217–221 (2006)

98. Shirasaki, K.; Yamamura, T.; Shiokawa, Y.: Electrolytic preparation, redox titration and stability of pentavalent state of uranyl tetraketone in dimethyl sulfoxide. *J. Alloys Comp.* **408–412**, 1296–1301 (2006)

99. Hasegawa, K.; Kimura, A.; Yamamura, T.; Shiokawa, Y.: Estimation of energy efficiency in neptunium redox flow batteries by the standard rate constants. *J. Phys. Chem. Solids* **66**, 593–595 (2005)

100. Xia, X.; Liu, H.T.; Liu, Y.: Studies of the feasibility of a Ce<sup>4+</sup>/Ce<sup>3+</sup>–V<sup>2+</sup>/V<sup>3+</sup> redox cell. *J. Electrochem. Soc.* **149**, A426–A430 (2002)

101. Chen, Y.D.; Santhanam, K.S.V.; Bard, A.J.: Solution redox couples for electrochemical energy storage. I. Iron(III)–Iron(II) complexes with O-phenanthroline and related ligands. *J. Electrochem. Soc.* **128**, 1460–1467 (1981)

102. Bae, C.H.: Cell Design and Electrolytes of a Novel Redox Flow Battery. PhD Thesis, UMIST, Manchester, pp. 1–215 (2001)

103. Chakrabarti, M.H.; Dryfe, R.A.W.; Roberts, E.P.L.: Evaluation of electrolytes for redox flow battery applications. *Electrochim. Acta* **52**, 2189–2195 (2007)

104. Bae, C.H.; Roberts, E.P.L.; Chakrabarti, M.H.; Saleem, M.: All-chromium redox flow battery for renewable energy storage. *Int. J. Green Energy* **8**, 248–264 (2011)

105. Liu, Q.; Shinkle, A.A.; Li, Y.; Monroe, C.W.; Thompson, L.; Sleightholme, A.E.S.: Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries. *Electrochim. Commun.* **12**, 1634–1637 (2010)

106. Liu, Q.; Sleightholme, A.E.S.; Shinkle, A.A.; Li, Y.; Thompson, L.T.: Non-aqueous vanadium acetylacetonate electrolyte for redox flow batteries. *Electrochim. Commun.* **11**, 2312–2315 (2009)

107. Shinkle, A.A.; Sleightholme, A.E.S.; Griffith, L.D.; Thompson, L.T.; Monroe, C.W.: Degradation mechanisms in the non-aqueous vanadium acetylacetonate redox flow battery. *J. Power Sources* **206**, 490–496 (2012)

108. Chakrabarti, M.H.; Roberts, E.P.L.; Bae, C.H.; Saleem, M.: Ruthenium based redox flow battery for solar energy storage. *Energy Conv. Manage.* **52**, 2501–2508 (2011)

109. Matsuda, Y.; Tanaka, K.; Okada, M.; Takasu, Y.; Morita, M.; Matsumura-Inoue, T.: A rechargeable redox battery utilizing ruthenium complexes with non-aqueous organic electrolyte. *J. Appl. Electrochem.* **18**, 909–914 (1988)

110. Chakrabarti, B.K.: Investigation of electrolytes for a novel Redox Flow Battery. PhD Thesis, UMIST, Manchester, pp. 1–250 (2003)

111. Chakrabarti, M.H.; Dryfe, R.A.W.; Roberts, E.P.L.: Organic electrolytes for redox flow batteries. *J. Chem. Soc. Pak.* **29**, 294–300 (2007)

112. Sleightholme, A.E.S.; Shinkle, A.A.; Liu, Q.; Li, Y.; Monroe, C.W.; Thompson, L.: Non-aqueous manganese acetylacetonate electrolyte for redox flow batteries. *J. Power Sources* **196**, 5742–5745 (2011)



113. Wen, Y.H.; Cheng, J.; Ma, P.H.; Yang, Y.S.: Bifunctional redox flow battery-1 V(III)/V(II)-glyoxal(O<sub>2</sub>) system. *Electrochim. Acta* **53**, 3514–3522 (2008)

114. Wen, Y.H.; Cheng, J.; Xun, Y.; Ma, P.H.; Yang, Y.S.: Bifunctional redox flow battery: 2. V(III)/V(II)-l-cystine(O<sub>2</sub>) system. *Electrochim. Acta* **53**, 6018–6023 (2008)

115. Xue, F.Q.; Wang, Y.L.; Wang, W.H.; Wang, X.D.: Investigation on the electrode process of the Mn(II)/Mn(III) couple in redox flow battery. *Electrochim. Acta* **53**, 6636–6642 (2008)

116. Cheng, J.; Zhang, L.; Yang, Y.S.; Wen, Y.H.; Cao, G.P.; Wang, X.D.: Preliminary study of single flow zinc-nickel battery. *Electrochim. Commun.* **9**, 2639–2642 (2007)

117. Xu, Y.; Wen, Y.H.; Cheng, J.; Cao, G.P.; Yang, Y.S.: A study of tiron in aqueous solutions for redox flow battery application. *Electrochim. Acta* **55**, 715–720 (2010)

118. Chakrabarti, M.H.; Roberts, E.P.L.: Electrochemical separation of ferro/ferricyanide using a membrane free redox flow cell. *NED Univ. J. Res.* **5**, 43–59 (2008)

119. Chakrabarti, M.H.; Roberts, E.P.L.: Analysis of mixtures of ferrocyanide and ferricyanide using UV-visible spectroscopy for characterization of a novel redox flow battery. *J. Chem. Soc. Pak.* **30**, 817–823 (2008)

120. Chakrabarti, M.H.; Roberts, E.P.L.; Saleem, M.: Charge–discharge performance of a novel undivided redox flow battery for renewable energy storage. *Intl. J. Green Energy* **7**, 445–460 (2010)

121. Bae, C.; Chakrabarti, H.; Roberts, E.: A membrane free electrochemical cell using porous Flow through graphite felt electrodes. *J. Appl. Electrochem.* **38**, 637–644 (2008)

122. Katayama, Y.; Konishiike, I.; Miura, T.; Kishi, T.: Redox reaction in 1-ethyl-3-methylimidazolium-iron chlorides molten salt system for battery application. *J. Power Sources* **109**, 327–332 (2002)

123. Wen, Y.H.; Zhang, H.M.; Qian, P.; Zhou, H.T.; Zhao, P.; Yi, B.L.; Yang, Y.S.: A study of the Fe(III)/Fe(II)-triethanolamine complex redox couple for redox flow battery application. *Electrochim. Acta* **51**, 3769–3775 (2006)

124. Kummer, J.T.; Oei, D.G.: A chemically regenerative redox fuel cell. II. *J. Appl. Electrochem.* **15**, 619–629 (1985)

125. Murthy, A.S.N.; Srivastava, T.: Fe(III)/Fe(II) ligand systems for use as negative half-cells in redox-flow cells. *J. Power Sources* **27**, 119–126 (1989)

126. Giner, J.D.; Stark, H.H.: Redox battery including a bromine positive electrode and a chromium ion negative electrode, and method. US Patent 4469760 (1984)

127. Saji, T.; Aoyagui, S.: Electron-transfer kinetics of transition-metal complexes in lower oxidation states. IV. Electrochemical electron-transfer rates of tris(2,2'bipyridine) complexes of iron, ruthenium, osmium, chromium, titanium, vanadium and molybdenum. *Electroanal. Chem.* **63**, 31–37 (1975)

128. Hosseiny, S.S.; Saakes, M.; Wessling, M.: A polyelectrolyte membrane-based vanadium/air redox flow battery. *Electrochim. Commun.* **13**, 751–754 (2011)

129. Hruska, L.W.; Savinell, R.F.: Investigation of factors affecting performance of the iron-redox battery. *J. Electrochem. Soc.* **128**, 18–25 (1981)

130. Wu, H.; Selman, R.J.; Hollandsworth, R.P.: Mass transfer and current distribution in a zinc/redox-battery flow cell. *Indian J. Tech.* **24**, 372–380 (1986)

131. Gonzalez, A.; Gallachoir, B.; McKeogh, E.; Lynch, K.: Study of electricity storage technologies and their potential to address wind energy intermittency in Ireland, May 2004. <http://www.seai.ie/uploadedfiles/FundedProgrammes/REHC03001FinalReport.pdf>. Accessed 25-05-2011 (2004)

132. Prudent Energy-case study: VRB Technology in Japan. [http://www.pdenergy.com/pdfs/casestudy\\_japan.pdf](http://www.pdenergy.com/pdfs/casestudy_japan.pdf). Accessed 28-5-2011

133. Tsekouras, G.; Anastasopoulos, C.; Kontargyri, V.; Kanellos, F.; Karanasiou, I.; Salis, A.; Mastorakis, N.: A demand side management program of vanadium redox energy storage system for an interconnected power system. In: Proceedings of the 2nd WSEAS/IASME International Conference on Energy Planning, Energy Saving, Environmental Education (EPESE'08), Corfu, Greece (2008)

134. Steeley, W.: VRB Energy Storage for Voltage Stabilization—Testing and Evaluation of the PacifiCorp Vanadium Redox Battery Energy Storage System at Castle Valley. EPRI Report 1008434. Technical Update. Utah (2005)

135. Skyllas-Kazacos, M.: Chapter on “Energy storage for stand-alone/hybrid systems: Electro-chemical Energy Storage Technologies” published in Stand-alone and Hybrid Wind Systems: Technology. Energy Storage and Applications Editor: Prof. J.K. Kalpellis. Woodhead Publishing (2010)

136. Skyllas-Kazacos, M.; Chakrabarti, M.H.; Hajimolana, S.A.; Mjalli, F.S.; Saleem, M.: Progress in flow battery research—a Review. *J. Electrochem. Soc.* **158**, R55–R79 (2011)

137. Premium Power website: <http://www.premiumpower.com/>. Accessed 26-5-2011

138. Redflow website: <http://www.redflow.com.au/>. Accessed 27-5-2011

139. Han, P.; Wang, H.; Liu, Z.; Chen, X.; Ma, W.; Yao, J.; Zhu, Y.; Cui, G.: Graphene oxide nanoplatelets as excellent electrochemical active materials for VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> and V<sup>2+</sup>/V<sup>3+</sup> redox couples for a vanadium redox flow battery. *Carbon* **49**, 693–700 (2011)

